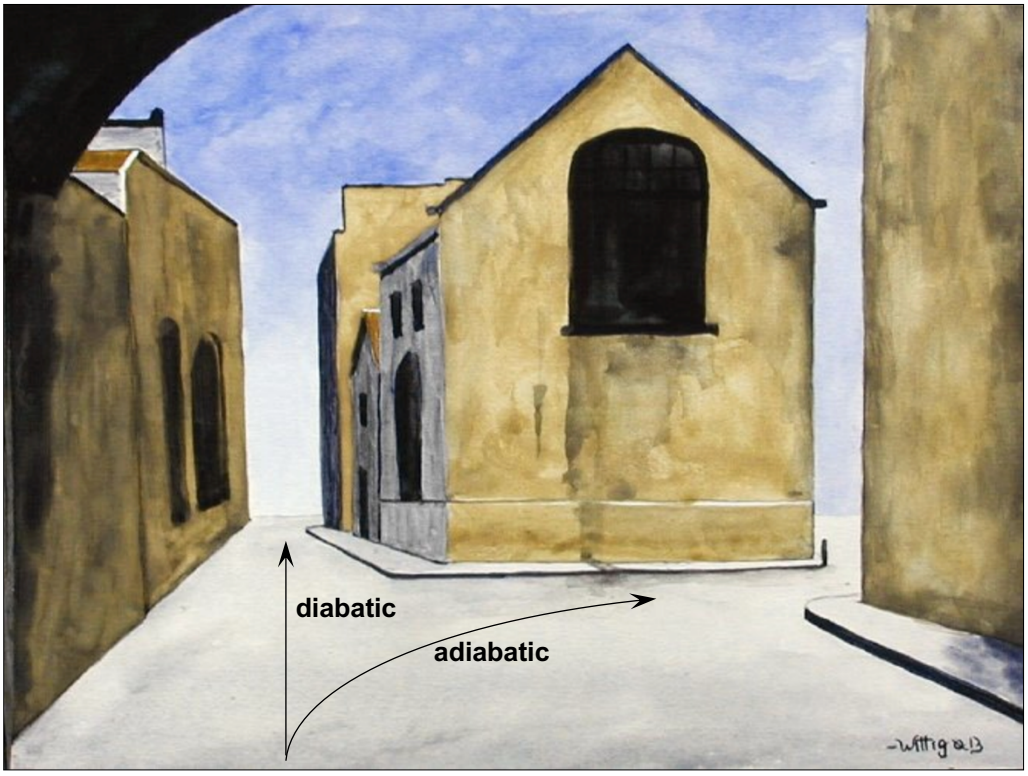
Part I. Chapter 4.

Landau-Zener Model



Tunnel Vision

Robert Wittig

"The difference between an optimist and a pessimist is that a pessimist sees problems in opportunities whereas an optimist sees opportunities in problems."

Winston Churchill

Contents

Appendix I.4.1. Non-Adiabatic Crossing of Energy Levels

Clarence Zener, Proc. Royal Soc. A, 696-702 (1932). Caution: this file can be read on the PDF but it is not printable. It is too dark and therefore the pages will print 100% black!

Preliminary Comments

In 1932 Clarence Zener and Lev Landau independently put forth the model for nonadiabatic transitions that bears their names. Ernst Stueckelberg also made a significant contribution.[1] Zener derived the exact solution to a 1D semiclassical model, and Landau did likewise, though in the perturbation limit and missing a factor of 2π. The model is referred to as Landau-Zener (at times, Landau-Zener-Stueckelberg). It is an important pedagogical tool that can yield useful insights and estimates for a broad range of systems. It is germane to the chemical dynamics of neutral species, where energy differences are rarely more than a few eV, and nuclei rarely travel faster than $2 \times 10^4\ m/s$. The model is fine for estimates and conceptual guidance, but it is not suitable for accurate calculations, at least not without significant modifications. The good news is that it is a straightforward, transparent steppingstone to more exacting studies.

Zener's 1932 paper is short and easy to follow. A pdf version is an appendix to this chapter. The background is dark, the text is fuzzy, and the pictures are hand drawn. It is the only version I could find. I tried to print it, but the pages came out 100% black due to the dark background, so you will likely read it from the pdf. Regardless, it is a *must read*.

In its 1D form, the model does not deal explicitly with the $\boldsymbol{g}-\boldsymbol{h}$ plane and the ICS. One can imagine a cross-sectional cut near a conical intersection. It is not always easy to assign effective mass, and the 1D coordinate can be interesting to the point of being vexing. Also, a given trajectory will sometimes encounter more than a single conical intersection. For example, it might encounter a seam on which lie an infinite number of cones and/or additional conical intersections that may either stand by themselves or lie on seams.

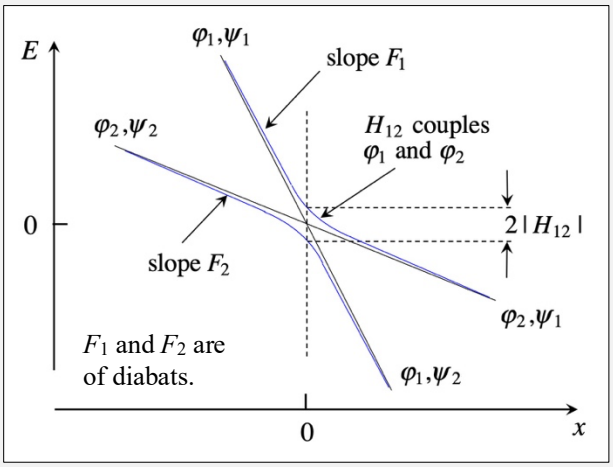


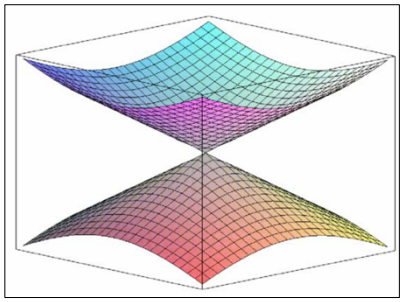
Figure 1. Well away from the crossing region, the adiabats ψ_i are identified with the diabats φ_i as follows: for $x << 0$, $\psi_1 = \varphi_1$ and $\psi_2 = \varphi_2$, whereas for $x >> 0$, $\psi_1 = \varphi_2$ and $\psi_2 = \varphi_1$. The diabats are coupled to one another by H_{12}, yielding the adiabats. The black and blue curves represent the diabats and adiabats, respectively. It is assumed that the kinetic energy of the 1D nuclear motion is much higher than the energy differences in the crossing region, in which case, $dx/dt = v$ is taken as being constant. Likewise, the slopes F_1 and F_2, which are each negative, are taken to be constant.

[1] L.D. Landau, Zur theorie der energieubertragung ii, Phys. Z. Sowjetunion, **2**, 46 (1932). C. Zener, Nonadiabatic crossing of energy levels, Proc. R. Soc. A **137**, 696 (1932). E.C.C. Stueckelberg, Theory of inelastic collisions between atoms, Helv. Phys. Acta **5**, 369 (1932).

A conceptual picture of how the 1D model works involves motion on a cross-sectional cut of a potential energy surface such as the ones discussed earlier for NH_3 and H_2O. It is assumed that this cut misses the intersection point. We will call its coordinate x, as indicated in Fig. 1. The coordinate x need not be simple. In fact, it is usually complicated except for very small systems. Along x, the diabats φ_1 and φ_2 cross, and when they are of the same symmetry, $H_{12} \neq 0$ and they couple to form two adiabats. To put this in the context of a conical intersection, e.g., on the NH_3 potential energy surface shown in Chapters 2 and 3, displacement of a coupling coordinate has lowered the symmetry that enabled the conical shape, yielding an avoided crossing. In any event, Fig. 1 depicts φ_1 and φ_2 coupling via H_{12} to yield the adiabats ψ_1 and ψ_2. The distance over which the diabats remain roughly constant (insofar as their orbital composition) is typically of order a Bohr radius, a_0. This is much larger than the effective crossing region where nonadiabatic dynamics transpire.

Referring to Fig. 1, it is assumed that the energy difference between the diabats, $E_{12} = E_1 - E_2$, is proportional to time, namely, $E_{12} = \alpha t$, where α is a constant, and t is set equal to zero at the crossing point for convenience. Because E_1 and E_2 have constant slopes, F_1 and F_2, the $E_{12} = \alpha t$ assumption is equivalent to assuming that the velocity v is constant, specifically, $\alpha = dE_{12} / dt = d(F_{12} x) / dt = vF_{12}$, where $F_{12} = F_1 - F_2$. Note that F_1 and F_2 are each negative and F_{12} is negative as well. The assumption of constant α is reasonable if the total energy is large enough that the velocity is approximately constant throughout the interaction region.

The assumption that F_1, F_2, and H_{12} are constant takes into consideration the fact that, for a diabatic basis, these parameters change over distances that are large relative to the length of the region where interaction is effective. Interaction ceases well away from the crossing region because the energy difference between the two diabats exceeds greatly the magnitude of the coupling matrix element. The model is semiclassical: electron degrees of freedom are treated quantum mechanically, whereas the nuclear degree of freedom is treated classically.



Referring to the conical intersection plot on the right, picture in your mind a vertical cross-sectional sheet that misses the origin and in so doing captures the essence of Fig. 1. The only difference is that in Fig. 1, the average energy of the diabats and adiabats changes with x, whereas the picture on the right has vertical cones, so the average energy is constant with respect to x. Figure 1 is appropriate to photodissociation or to two atoms undergoing a collisional interaction. With the former, the system progresses from left to right. With the latter, the system progresses initially from right to left. However, by definition, the one-dimensional collision is head-on, so the pair turns around and then dissociates from left to right. The trajectory does not end where it started, however, because nonadiabatic coupling causes some of the flux to switch adiabats.

I will work through the 1D Landau-Zener model with the goal of building intuition and establishing relationships between the model's physical content and observables, albeit in a highly simplified pedagogical model. Then the switch. You may think that going from

1D to 2D incurs modest change. After all, neither 1D nor 2D is realistic, as the space we live in is 3D. That is not how to think about it, however. The 2D space is that of the $\boldsymbol{g}-\boldsymbol{h}$ plane. It can accommodate polyatomic molecules that display a conical intersection. The conical intersection presents a hierarchical picture in the sense that it assigns privileged status to two degrees of freedom out of many. The dynamics of the polyatomic system, say following a nonadiabatic transition, can involve a high percentage of the polyatomic molecule's nuclear phase space on a lower potential energy surface.

1. Equation of Motion

The fact that v is constant and F_1 and F_2 are each constant ensures that $\alpha = vF_{12}$ is constant. As mentioned above, for the situation depicted in Fig. 1, F_{12} and α are each negative. With E_1 and E_2 well defined at each instant of time (instantaneous eigenvalues), the Schrödinger equation is

$$H\left\{A\varphi_1 \exp\left(-i\int_{t_0}^{t} dt' E_1\right) + B\varphi_2 \exp\left(-i\int_{t_0}^{t} dt' E_2\right)\right\} =$$

$$i\left\{\left(\dot{A} - iAE_1\right)\varphi_1 \exp\left(-i\int_{t_0}^{t} dt' E_1\right) + \left(\dot{B} - iBE_2\right)\varphi_2 \exp\left(-i\int_{t_0}^{t} dt' E_2\right)\right\}, \qquad (4.1)$$

where $\hbar = 1$ is used.

Figure 1' is a closeup of the Fig. 1 origin region. It indicates that E_{12} varies linearly with time. It is equal to the slope difference: $F_{12} = F_{11} - F_2$, times the displacement x, where $x = vt$. We define $t = 0$ as the time when left to right transit at speed v reaches $x = 0$, where the diabats cross. In this case, t is negative for $x < 0$ and positive for $x > 0$. Thus, $E_{12} = tvF_{12}$. Note that $E_{12}(t)$ is positive for $x < 0$ and negative for $x > 0$. Other conventions for labeling the time axis are available. I chose the one in Fig. 1' because it focuses on the region of crossing of the diabats rather than the asymptotic hyperbolic adiabatic curves.

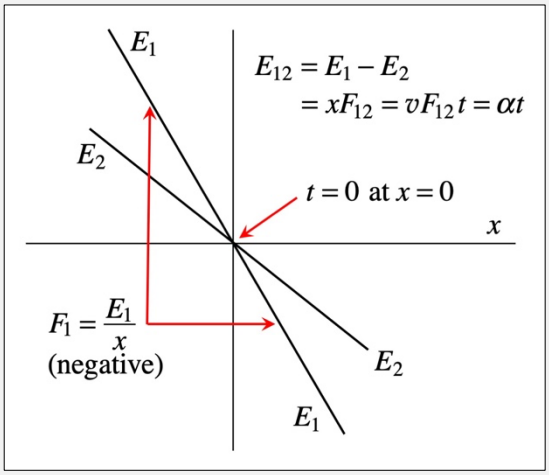


Figure 1'. Closeup of Fig. 1 origin region: The system proceeds from left to right. $E_{12} > 0$ for $x < 0$ and $E_{12} < 0$ for $x > 0$.

The right-hand side of eqn (4.1) treats the diabats φ_1 and φ_2 as being time independent. But how accurate is the assumption that $\dot{\varphi}_1 = v\nabla\varphi_1$ and $\dot{\varphi}_2 = v\nabla\varphi_2$ can be neglected? To get an idea of how large such contributions might be, multiply $v\nabla\varphi_1$ from the left by φ_1^* and integrate over electron coor-

dinates to obtain $v\langle\varphi_1|\nabla\varphi_1\rangle$. Using the rough estimate: $\nabla\varphi_1 \sim \varphi_1 / x_0$, yields $v\langle\varphi_1|\nabla\varphi_1\rangle \sim \hbar v / x_0$ (with explicit $\hbar$). For $v = 300\ m/s$ and $x_0 = 1$ Å, $\hbar v / x_0$ has a value of 36 cm^{-1}. This is small enough to neglect, in most cases.

With $H = H_0 + H'$, the coupling of φ_1 and φ_2 is due to H', which is assumed to have no nonzero diagonal matrix elements. The perturbation H' serves only to couple the diabats. The diagonal matrix elements of H_0 are E_1 and E_2, and A and B are time dependent coefficients whose squares, $|A|^2$ and $|B|^2$, are the proportions of φ_1 and φ_2 in the adiabatic wavefunctions, respectively. Integrals are from a reference time t_0 (in the distant past) to the time of observation. If there *are* nonzero diagonal matrix elements, they can be transferred to the energies. It is assumed that they are too small to worry about.

Nonadiabatic transitions were discussed earlier from the perspective of the adiabats. Rapid nuclear motion does not provide enough time for the electrons to readjust completely along the nuclear trajectory, so the diabatic pathway is followed, to some extent. In the Landau-Zener model, the nonadiabatic transition is calculated using the diabatic representation. As the system traverses the interaction region, the H_{12} matrix element can be effective if it has sufficient time to act. This simple reasoning will appear in the result in a transparent way.

Multiplying eqn (4.1) from the left alternately by φ_1^* and φ_2^* and integrating over electron coordinates yields

$$\dot{A} = -iH_{12}B\exp\left(i\int_{t_0}^{t} dt' E_{12}\right) \tag{4.2}$$

$$\dot{B} = -iH_{21}A\exp\left(-i\int_{t_0}^{t} dt' E_{12}\right). \tag{4.3}$$

You should carry out the algebra that leads to eqns (4.2) and (4.3) yourself to ensure that you see how the math works. To uncouple these equations, first differentiate, using the Leibniz rule for differentiation of an integral:

$$\frac{d}{d\alpha}\int_{a(\alpha)}^{b(\alpha)} dx\, f(x,\alpha) = \frac{d\,b(\alpha)}{d\alpha} f\big(b(\alpha),\alpha\big) - \frac{d\,a(\alpha)}{d\alpha} f\big(a(\alpha),\alpha\big) + \int_{a(\alpha)}^{b(\alpha)} dx\, \partial_\alpha f(x,\alpha)$$

to obtain

$$\ddot{A} = -iH_{12}\left(\dot{B} + iBE_{12}\right)\exp\left(i\int_{t_0}^{t} dt' E_{12}\right) \tag{4.4}$$

$$\ddot{B} = -iH_{21}\left(\dot{A} - iAE_{12}\right)\exp\left(-i\int_{t_0}^{t} dt' E_{12}\right). \tag{4.5}$$

We then make substitutions to obtain differential equations for the coefficients A and B. For example, putting $\dot{A}$ from eqn (4.2) and A from eqn (4.3) into eqn (4.5) yields a useful expression for $\ddot{B}$. This requires attention to detail. Only one of the coefficients is needed, as the other is obtained from $|A|^2 + |B|^2 = 1$. In this way, we arrive at the so-called Weber equation (which dates to 1869):

$$\ddot{B} + iv F_{12} t \dot{B} + |H_{12}|^2 B = 0 \,. \tag{4.6}$$

The desired quantity is B after all interaction has ceased, i.e., $B \to B_f$. This may not *always* be the "desired quantity," as one may wish to have $B(t)$ throughout the trajectory. It is *nearly always* the case, however. Zener recognized eqn (4.6) as the Weber equation, which has a closed form solution, yielding $B(t)$. Asymptotic limits then yield the amplitude B_f for starting in φ_2 and still being in φ_2 after interaction has ceased. This is how the Landau-Zener model was solved from the time of its introduction in 1932 until 2005.[2]

Even though $B(t)$ yields the desired quantity B_f, it is not necessary to obtain $B(t)$ if only B_f is required. Indeed, B_f will now be obtained directly.

2. Contour Integration

Let's start with eqn (4.6) [$\ddot{B} + iv F_{12} t \dot{B} + |H_{12}|^2 B = 0$] and divide it by B. This does not introduce a singularity because B never achieves a value of zero. Integration from $t = -\infty$ to $t = +\infty$ (corresponding to going from $B = 1$ to $B = B_f$, respectively) yields

$$\int_{-\infty}^{+\infty} dt \left(\frac{\ddot{B}}{B} + iv F_{12} t \frac{\dot{B}}{B} + |H_{12}|^2 = 0 \right) \Rightarrow \int_{-\infty}^{+\infty} dt \left(\frac{i}{v F_{12}} \frac{\ddot{B}/B + |H_{12}|^2}{t} = \frac{\dot{B}}{B} \right). \tag{4.7}$$

The time integration of $dt\,\dot{B}/B$ from $t = -\infty$ to $t = +\infty$ is now replaced with the integration of dB/B from $B = 1$ to $B = B_f$. This enables eqn (4.7) to be written

$$\int_{B=1}^{B=B_f} \frac{dB}{B} = \ln B_f = \frac{i}{v F_{12}} \int_{-\infty}^{+\infty} dt \left(\frac{\ddot{B}/B + |H_{12}|^2}{t} \right) \tag{4.8}$$

It remains to carry out the integration on the right-hand side.

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[2] C. Wittig, The Landau-Zener Formula, J. Phys. Chem. B **109**, 8428 (2005). A.I. Chichinin, streamlined my version: A.I. Chichinin, Wittig's Approach to Landau-Zener Made Even Simpler, J. Phys. Chem. B **117**, 6018 (2013). The derivation in this chapter is streamlined yet further, as well as being extended to 2D in the form of the $\boldsymbol{g}$ – $\boldsymbol{h}$ plane.

Equation (4.6) gives $\ddot{B}/B + |H_{12}|^2 = 0$ at $t = 0$. Consequently, the parenthetic term in eqn (4.8) does not have a pole at $t = 0$.[3] The right-hand side of eqn (4.8) cannot be integrated as it stands because $\ddot{B}/B$ is unknown. This motivates contour integration in the complex t plane (Fig. 2). You should complete the exercise below before working your way through the contour integration. The fact that the parenthetic term does not have a pole at $t = 0$ is a great help. Indeed, the fact that the contour in Fig. 2 encloses no pole, means that the straight-line integration path ($t = -\infty \rightarrow +\infty$) and the counterclockwise semicircular integration sum to zero. Consequently, the $\ln B_f$ term in eqn (4.8) is given by

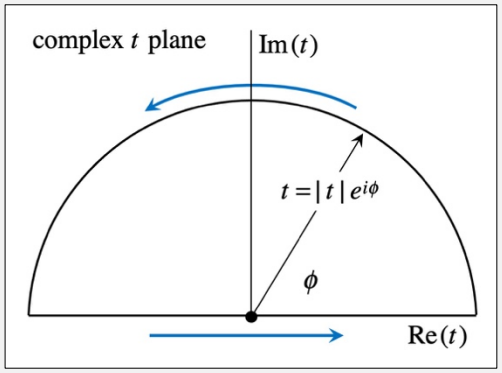


Figure 2. The parenthetic term in eqn (4.8) is integrated over semicircular and straight-line portions. The limit $|t| \rightarrow \infty$ is taken.

$$\ln B_f = -\frac{i}{vF_{12}} \lim_{|t|\rightarrow\infty} \int_{\phi=0}^{\phi=\pi} |t| e^{i\phi} i\, d\phi \left(\frac{\ddot{B}/B + |H_{12}|^2}{|t| e^{i\phi}} \right). \tag{4.9}$$

The fact that all nonadiabatic interaction ceases far from the crossing region means that $\ddot{B}/B \rightarrow 0$ as $|t| \rightarrow \infty$ on the semicircular path. The $|H_{12}|^2$ term is taken outside the integral, and the two $|t| e^{i\phi}$ terms inside the integral cancel one another. Finally, the fact that $\ddot{B}/B$ vanishes on the $|t| \rightarrow \infty$ semicircle yields

$$\ln B_f = \frac{\pi |H_{12}|^2}{vF_{12}} \implies B_f = \exp\left(-\frac{\pi |H_{12}|^2}{\hbar v |F_{12}|} \right). \tag{4.10}$$

The fact that F_{12} is negative has been used, and explicit $\hbar$ has been added.

Exercise: (challenging) Show mathematically that $\ddot{B}/B \rightarrow 0$ as $|t| \rightarrow \infty$. Start by solving eqn (4.6) in the large-t limit with $\ddot{B}$ set to zero. Explain why it is acceptable to do this. Use the resulting expression for $B(t)$ to show that $\ddot{B}$ varies as t^{-2} in the large-t regime, and consequently $\ddot{B}$ vanishes as $t \rightarrow \infty$. This is important in the contour integration because it ensures convergence at $\pm\infty$.

[3] I recommend the excellent text on complex analysis by James Brown and Ruel Churchill: Complex Variables and Applications (McGraw-Hill, 8th Edition, 2009).

3. Interpretation

The nonadiabatic transition probability is equal to the squared modulus of B_f:

$$P(\psi_2 \rightarrow \psi_1) = P(\varphi_2 \rightarrow \varphi_2) = |B_f|^2 = \exp\left(-\frac{2\pi |H_{12}|^2}{\hbar v |F_{12}|}\right). \tag{4.11}$$

The dependencies with respect to $|H_{12}|$, v, and $|F_{12}|$ are intuitive: (i) increasing $|H_{12}|$ increases the energy separation of the adiabats and therefore the likelihood that the system remains adiabatic; (ii) large v facilitates nonadiabaticity; (iii) the dependence on the change of slope reflects the well-known fact that physical systems try to avoid impulsive momentum changes.

The physically motivated definitions $\omega_{12} = |H_{12}|/\hbar$ and $\tau_d = |H_{12}| \,/\, v\,|F_{12}|$ yield

$$P(\psi_2 \rightarrow \psi_1) = \exp\left(-2\pi\,\omega_{12}\,\tau_d\right). \tag{4.12}$$

The time interval over which the system is near $x = 0$ can be written $\tau_d = l/v$, where l is some interaction length. Obtaining a value for the length parameter l often involves nothing more sophisticated than an educated guess of the effective distance over which interaction takes place. Referring to Fig. 1, this length can be estimated (very roughly) by equating $|H_{12}|$ to the magnitude of the energy difference, which is $|F_{12}|$ times l. Thus, τ_d is taken to be $\sim |H_{12}|/(v\,|F_{12}|)$. The product $\omega_{12}\tau_d$ is a figure of merit: large τ_d (slow passage) and large ω_{12} (widely separated adiabatic curves) promote adiabaticity.

For the sake of concreteness, consider a diatom. There is an avoided crossing when the intersecting zero-order (diabatic) curves are of the same symmetry in the molecule based reference system that excludes rotation. For curves of different symmetry in this molecule based reference system, rotation can bring about interaction. For example, spin-rotation interaction can yield large matrix elements between electronic states of different symmetry for the large values of orbital angular momentum that occur in atom-atom collisions. In spectroscopy, spin-rotation interaction is usually small. However, the matrix elements are proportional to $[L(L+1)]^{1/2}$, so the effect can be pronounced in a collision of a fast light atom with, say, a heavy target atom, leading to efficient nonadiabatic coupling.

Cute formula

Figure 1, with reaction proceeding from left to right, is appropriate for photodissociation, for example, a diatom excited to a repulsive potential from which it dissociates via a region of avoided crossing. Of course, the same physics applies to the corresponding collision in which the trajectory goes from right to left. In this case the system traverses $x = 0$ twice: on the way in and, after turning around when it encounters the repulsive potential, on the way out. An interesting formula is obtained by considering this double pass through the interaction region.

Assume the system starts on ψ_1 far to the right. In the first pass through the crossing region, the probability that a nonadiabatic transition from ψ_1 to ψ_2 has taken place is P. The probability that the system stays on ψ_1 is $1- P$. After the respective turning points are reached on each adiabat (not indicated in Fig. 1), the trajectories proceed to the right. The probability that ψ_2 stays on ψ_2 is $1 - P$, while the probability that ψ_1 makes a transition to ψ_2 is P. Thus, the total probability that the system has undergone a nonadiabatic transition is given by

$$\begin{aligned} P_{net} &= P(\psi_1 \to \psi_2)\,P(\psi_2 \to \psi_2) + P(\psi_1 \to \psi_1)\,P(\psi_1 \to \psi_2) \\ &= P\big(1-P\big) + \big(1-P\big)P \\ &= 2P\big(1-P\big) \end{aligned} \tag{4.13}$$

This is the probability that an incident trajectory (right to left in Fig. 1) on either adiabat has undergone a nonadiabatic transition after passing through the crossing region on the way out. It is cute but only applicable to 1D.

4. Two-Dimensional Landau-Zener Model

The Landau-Zener 1D dynamics model is now extended to two dimensions, specifically, those of the $\boldsymbol{g}-\boldsymbol{h}$ plane. This is a big deal. It opens the door to polyatomic molecules having any number of nuclear degrees of freedom, only two of which are usually needed to tune the system to a point of degeneracy, i.e., a conical intersection.

There are significant differences between the 1D and 2D models. In the former, the coupling matrix element in the diabatic basis, H_{12}, is taken as constant throughout the region of interest. Recall that it is not feasible to tune both H_{12} and the energy separation between diabats, $H_{11}-H_{22}$, by varying the single nuclear coordinate. One can vary H_{12} until it is zero, but $H_{11}-H_{22}$ is highly unlikely to also be zero at these nuclear coordinates. Likewise, when $H_{11}-H_{22}$ is varied until it is zero, it is highly unlikely that H_{12} will also be zero. Moreover, it is known from experiment and theory that the assumption of constant H_{12} usually describes avoided crossings in diatoms with acceptable accuracy, so one should forget about tuning H_{12}.

On the other hand, in the case of the $\boldsymbol{g}-\boldsymbol{h}$ plane, the matrix elements H_{12} and $H_{11}-H_{22}$ can each be tuned to zero through variation of the nuclear coordinates. If H_{12} and the difference between the diagonal matrix elements, $H_{11}-H_{22}$, each vanishes at the same nuclear configuration, there is degeneracy of the electronic states in both the diabatic and adiabatic representations. This is the familiar conical intersection.

For a conical intersection, both $H_{11}-H_{22}$ and H_{12} vary linearly with displacement from the degeneracy point, in contrast to the 1D example of Sections 1 – 3, where H_{12} was taken as being constant. When adiabats intersect, nonadiabatic coupling in the region of the intersection is facilitated, enabling even modest nuclear motions to promote nonadiabatic transitions. Think of it this way. Nuclear motion imprints a relatively slow time variation on electron wavefunctions. They are modulated through this nuclear motion. Far from degeneracy this goes unnoticed. However, when the electronic states are close in energy, this imprinted time dependence has a spectrum that is in registry with the spectrum of transition frequencies between the electronic states. Said differently, the Fourier spectrum of the nuclear motion overlaps to a significant extent the spectrum of electronic transition frequencies. We will focus on the region of conical intersection.

Features of the conical intersection region discussed in Chapter 3 are germane to the development of a 2D model of the nonadiabatic dynamics. When there is a conical intersection, the tuning and coupling coordinates lie in the $\boldsymbol{g}-\boldsymbol{h}$ plane, with the degeneracy point being the origin. We have seen that, in a diabatic basis, coordinate axes can be defined according to the directions of the gradients: $\boldsymbol{g} = \frac{1}{2}\nabla(H_{11}-H_{22})$ and $\boldsymbol{h} = \nabla H_{12}$.[4] There is also an important vector $\boldsymbol{s}$, the gradient of the average energy: $\boldsymbol{s} = \frac{1}{2}\nabla(H_{11}+H_{22})$. It is unaffected by the orthogonal rotation of the ∇H_e matrix, so it is often put to the side. It is responsible for the tilt of conical intersections, and we need to keep this in mind.

[4] These directions are unlikely to be orthogonal at the outset. As discussed in Chapter .3, orthogonal axes are obtained by rotating the diabatic basis.

We will be dealing with the $\boldsymbol{g}-\boldsymbol{h}$ plane a great deal in what follows. Thus, I recommend strongly that you review the relevant parts of Chapters 2 and 3. This will take a serious amount of time, but you will not regret it.

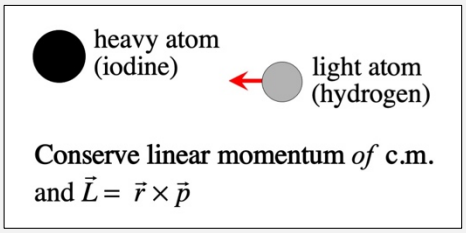
To proceed, take x to be displacement along the direction of $\boldsymbol{g}$; likewise, y is displacement along the direction of $\boldsymbol{h}$. The coordinates x and y are not easily visualized in terms of nuclear displacements except in special cases. The electronic Hamiltonian matrix is given by

$$H_e' = \begin{pmatrix} gx & iA_{\mathrm{so}} + hy \\ -iA_{\mathrm{so}} + hy & -gx \end{pmatrix}, \tag{4.14}$$

where $g = |\,\boldsymbol{g}\,|$, $h = |\,\boldsymbol{h}\,|$, and the $\pm iA_{\mathrm{SO}}$ terms are due to spin-orbit interaction, as explained in Appendix .2.1. The average energy sx where $\boldsymbol{s} = \tfrac{1}{2}\nabla(H_{11}+H_{22})$, is suppressed in eqn (4.14). This is indicated with a prime. This average energy can be reinstated at any time. Indeed, without it the cones are not tilted, whereas the cones *are* tilted in a high percentage of conical intersections. It is assumed that the $\pm iA_{\mathrm{SO}}$ terms do not depend on x and/or y because spin-orbit interaction depends only weakly on nuclear displacement. Consequently, it cannot be eliminated through the tuning of nuclear coordinates that is used to eliminate the real part of the off-diagonal matrix elements in the diabatic basis, hy.

Spin-orbit interaction has been excluded until now to simplify matters and because it plays a minor role in many systems. Its role in potential energy surface intersections is discussed at some length in Appendix I.2.1. *Time Reversal Symmetry and Intersection Conditions*, where the fact that its coupling matrix element is purely imaginary is explained. Appendix I.2.1 is lengthy, so right now we will assume that the spin-orbit matrix elements can be written $\pm iA_{\mathrm{SO}}$.

Figure 3. There are six degrees of freedom for two structureless atoms in 3D. Conserved quantities are three degrees of freedom for linear momentum and one degree of freedom for orbital angular momentum. A nice example is a hydrogen atom scattering from an iodine atom.



For a system with only two nuclear degrees of freedom (Fig. 3), the dimension of the ICS is zero without the inclusion of spin-orbit interaction. When spin-orbit interaction is included, the surfaces cannot intersect conically, as the system cannot be tuned in the $\boldsymbol{g}-\boldsymbol{h}$ plane to satisfy simultaneously the requirements: $H_{11}-H_{22} = 0$, $\mathrm{Re}\,H_{12} = 0$, and $\mathrm{Im}\,H_{12} = 0$. As mentioned above, an important point is that the spin-orbit interaction term $\mathrm{Im}\,H_{12}$ varies weakly with nuclear displacement. This means avoided crossing type behavior applies to systems whose nuclear space is of arbitrarily large dimension. Indeed, the inclusion of spin-orbit interaction in the model discussed here will illustrate how it affects intersections and near intersections of adiabatic potentials. The way it influences nonadiabatic transitions will (hopefully) become apparent, albeit at an unsophisticated level

Polyatomic species might have many nuclear degrees of freedom, in which case finding three tuning coordinates is possible in principle. Also, as discussed in Appendix .2.1, there are cases for which five or more tuning coordinates are needed. The case of three tuning coordinates can be dealt with using vector calculus, whereas five and more tuning coordinates can still be handled geometrically, but with higher level mathematics (differential geometry, geometric algebra, etc.). Even when only three coordinates need to be varied, the nice picture of two cones sharing a common apex (double cones) is no longer applicable.

The two eigenvalues of eqn (4.14) are

$$E_{1(2)} = \pm \left(A_{SO}{}^2 + (gx)^2 + (hy)^2 \right)^{1/2}. \tag{4.15}$$

These adiabats are vertical double cones when $A_{SO} = 0$. Otherwise, they are hyperboloids for which there is no intersection. This was discussed near the end of Chapter .3. The eigenvalues at $x = 0$ and $y = 0$ are $\pm A_{SO}$. Had $\boldsymbol{s}$ been included, the cones would have been tilted. Figure 4 illustrates the effect of the spin-orbit term for vertical cones.

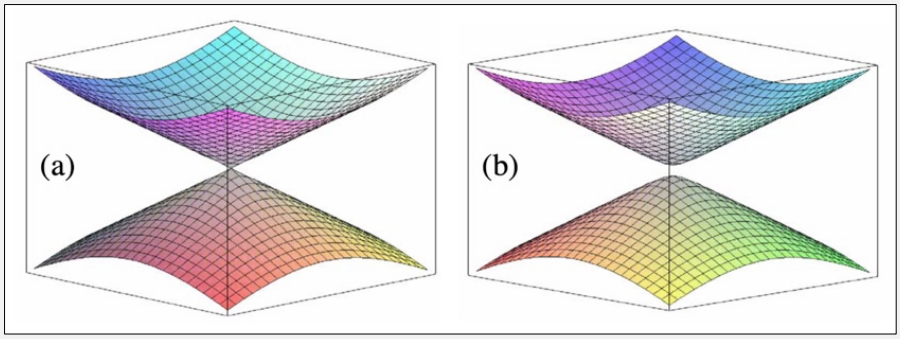


Figure 4. Plots of eqn (4.15): (a) $A_{SO} = 0$; (b) $A_{SO} \neq 0$. In (b), the surfaces are hyperboloids that do not intersect. Scaling enables a vertical axis of symmetry. The gap between their extrema has a magnitude of $2|A_{SO}|$.

The fact that displacement appears in the off-diagonal position in eqn (4.14) (specifically, the y in the hy term) tells us that to treat the dynamics the H_e matrix must be transformed. Otherwise, it will not be possible to converge the solutions at long times. With x and y each varying linearly with time according to the velocity components ($x = x_0 + v_x t$ and $y = y_0 + v_y t$), the long-time limit of H_e is proportional to time

$$H_e \xrightarrow{\text{large } t} \begin{pmatrix} gv_x & hv_y \\ hv_y & -gv_x \end{pmatrix} t, \tag{4.16}$$

where x_0 and y_0 have been suppressed for convenience.

This makes no sense because it states that interaction never ceases. This is a mathematical problem that arises because the conical intersection region is extended beyond its domain of validity. The conical shape is local to the region of intersection. At long times the part of the surface being sampled is not at all conical, and in this region eqn (4.16) is not applicable.

In the 1D Landau-Zener model, no such difficulty arose. In that case, maintaining a constant coupling matrix element while the energy difference grows linearly with time automatically localizes the interaction to the region of the curve crossing. Think of the time behavior in eqn (4.16) as a consequence of the mathematical prescription that is used to describe the conical variation that exists near the origin.

Rotation of the basis by just the right amount will eliminate the time dependence of the off-diagonal matrix elements, whereas the diagonal matrix elements will remain time dependent. The resulting Hamiltonian matrix is then expressed in terms of spin-orbit coupling, parameters that define the trajectories, and displacements in the $\boldsymbol{g} - \boldsymbol{h}$ plane. For a given trajectory, the transition probability assumes a form like that in eqn (4.11). That will be discussed in Section 6. Right now, let's see how the rotation of the basis plays out.[5]

5. Rotating the Basis

Orthogonal rotation of the diabatic basis will be used to eliminate the time dependence of the off-diagonal matrix element. It will not eliminate the time dependence of the diagonal matrix elements. That would be impossible. Think of it this way. Eliminating the time dependence of both the off-diagonal and the diagonal matrix elements would render the Landau-Zener model time independent, which is nuts. Our intention is to formulate the 2D model such that it corresponds as closely as possible to the 1D model. The fact that $E_{12} = \alpha t$ in the 1D model means that this time dependence, or something close to it, should be present in the 2D model.

The spin-orbit terms $\pm iA_{SO}$ in the off-diagonal positions are unaffected by the rotational transformation. This is because the transformation is orthogonal, whereas a unitary transformation is required to diagonalize a complex matrix. It turns out that the spin-orbit part of the matrix does not rotate. The expert explains how this works in the box below. The rotated part of the electronic Hamiltonian matrix (i.e., leaving aside the diagonal *sx* terms, which do not rotate) is given by

$$H_e \Longrightarrow H_e' = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} gx & iA_{so} + hy \\ -iA_{so} + hy & -gx \end{pmatrix} \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}. \qquad (4.17)$$

We will focus on this rotational transformation.

---

[5] Even when $A_{SO} = 0$, there are significant differences between the 1D and 2D cases in the region $x \approx 0$ and $y \approx 0$. The adiabats can intersect, but trajectories do not really pass through the degeneracy point (origin of the $\boldsymbol{g}-\boldsymbol{h}$ plane). They can come close but, being a point, the origin has zero area. With two degrees of freedom, it is the *vicinity* of the degeneracy point that is germane to the nonadiabatic dynamics.

Referring to eqn (4.17), the middle matrix is written

$$\begin{pmatrix} gx & hy \\ hy & -gx \end{pmatrix} - A_{\rm so}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix},$$

The second term is $-A_{\rm so}\sigma_2$. The orthogonal transformation matrix can be written

$$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\cos\theta + i\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\sin\theta = \mathbf{1}\cos\theta + i\sigma_2\sin\theta\,.$$

Thus, the matrix $A_{\rm so}\sigma_2$ commutes with the orthogonal matrix, so the orthogonal transformation leaves the imaginary off-diagonal terms alone.

the expert

A specific value of θ is needed eliminate the time dependence of the off-diagonal terms. The facts that the trace of the middle matrix is zero and that trace is conserved in an orthogonal transformation will prove helpful insofar as the diagonals are concerned. There are only two independent matrix entries. The off-diagonal matrix elements are Hermitian adjoints of one another, and the diagonal matrix elements are related via the trace. This value of θ defines the transformation in terms of the $\boldsymbol{g}-\boldsymbol{h}$ plane and dynamical processes that transpire therein.

This transformation was introduced in Chapter 1 to switch back and forth between adiabatic and diabatic representations. The criterion that defined the value of θ was the elimination, to the extent possible, of the derivative coupling matrix element in the diabatic basis, ideally, $\langle\varphi|\nabla\varphi\rangle = 0$. This served as the definition of the diabatic basis. The same basic strategy is used here, except now the criterion is elimination of the time dependence of the off-diagonal matrix element. The amount of rotation needed to achieve this leaves the system in a representation that is neither 100% adiabatic nor 100% diabatic. The diagonal terms *sx* do not rotate. That is why they were left out of eqn (4.17).

An important point to keep in mind is that it is necessary to deal with the *transformed* matrix elements, namely, the ones in which the time dependence of H_{12} has been eliminated, not the ones that we began with. In Zener's 1932 paper, it was assumed that the coupling matrix element is time independent, and we will accede to his assumption. As mentioned above, the trace of the middle matrix in eqn (4.17) is zero, so for the two diagonal matrix elements, we need only work with $(H_e')_{11}$, as $(H_e')_{22}$ differs only by a sign due to trace invariance. Likewise, $(H_e')_{12} = (H_e')_{21}{}^{\dagger}$. Thus, the transformation is written

$$R(\theta)\begin{bmatrix} gx & iA_{\rm so}+hy \\ -iA_{\rm so}+hy & -gx \end{bmatrix}R(\theta)^{-1} = \begin{bmatrix} (H_e')_{11} & (H_e')_{12} \\ (H_e')_{12} & (H_e')_{22} \end{bmatrix}. \qquad (4.17')$$

The rotation angle θ in eqn (4.17) is related to the nuclear coordinates. For example, if the off-diagonal matrix elements could be eliminated, we would have adiabats. As it stands, the rotated system given by eqn (4.17) is close to an adiabatic representation if the spin-orbit term is small. In general, this rotation creates a mixed system that is neither fully diabatic nor fully adiabatic. The material that follows requires a nontrivial amount of algebra. When lengthy manipulations and derivations arise, I will give results but not the many algebraic steps. Belaboring the math would not work. In any event, let's get going.

Carrying out the matrix multiplications in eqn (4.17) yields

$$(H_e')_{11} = gx\cos 2\theta + hy\sin 2\theta \tag{4.18}$$

$$(H_e')_{12} = -gx\sin 2\theta + hy\cos 2\theta + iA_{so}\,. \tag{4.19}$$

If we assume that the velocity along the trajectory remains constant throughout the region where coupling takes place, the displacements x and y can be written

$$x = x_0 + v_x t \tag{4.20}$$

$$y = y_0 + v_y t. \tag{4.21}$$

The assumption of a constant velocity is consistent with our ansatz of a sufficiently high incoming translational momentum that its fractional change in passing through the interaction region is small. This is probably (possibly) the same reasoning that led Zener to the assumption $E_{12} = \alpha t$.

The parameters x_0 and y_0 are necessary because x and y do not in general pass through their zeros at the same time. In other words, the origin is missed. These parameters account for the fact that, along a given trajectory, the energy difference can be decreasing while at the same time the coupling matrix element is increasing, or *vice versa*. The parameters x_0, y_0, v_x, and v_y, in concert with g and h completely define the trajectory.

The coordinates x and y are time dependent according to eqns (4.20) and (4.21). As mentioned above, we wish to eliminate the time dependence of $(H_e')_{12}$ but not the time dependence of $(H_e')_{11}$. After all, we cannot get rid of *all* time dependence! Thus, we will begin by finding the value of θ that eliminates the time dependence of the off-diagonal elements and then introduce this value of θ into the expression for $(H_e')_{11}$.

To carry out the math, x and y in eqns (4.20) and (4.21) are put into eqn (4.19) and the resulting expression is separated into time-independent and time-dependent parts:

$$(H_e')_{12} = iA_{so} - g\left(x_0 + v_x t\right)\sin 2\theta + h\left(y_0 + v_y t\right)\cos 2\theta \tag{4.22}$$

$$= iA_{so} - gx_0\sin 2\theta + hy_0\cos 2\theta + \underbrace{\left(hv_y\cos 2\theta - gv_x\sin 2\theta\right)}_{0} t\,. \tag{4.23}$$

Setting the coefficient of t to zero yields the expression for the required value of θ, namely,

$$\tan 2\theta = \frac{hv_y}{gv_x}. \tag{4.24}$$

Figure 5 is a great help. It enables $\sin 2\theta$ and $\cos 2\theta$ in eqn (4.23) to be replaced straightaway with parameters that define the trajectory and couplings. [Pictures in general can be a great help.] Minor algebra yields

$$(H_e')_{12} = iA_{\text{so}} + \frac{gh\left(v_x y_0 - v_y x_0\right)}{\left((gv_x)^2 + (hv_y)^2\right)^{1/2}}. \tag{4.25}$$

In a similar vein, eqns (4.20), (4.21), and (4.24) are now imported into the expression for $(H_e')_{11}$ given by eqn (4.18). This step makes use of the convenient right triangle relations given by Fig. 5. It requires a nontrivial amount of algebraic manipulation. At least it did when I carried it out. The result is

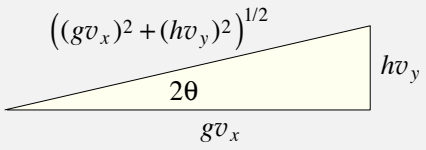


Figure 5. Triangle relation for eqn (4.24).

$$(H_e')_{11} = \left((gv_x)^2 + (hv_y)^2\right)^{1/2} t + \frac{g^2 v_x x_0 + h^2 v_y y_0}{\left((gv_x)^2 + (hv_y)^2\right)^{1/2}}. \tag{4.26}$$

Thus, $(H_e')_{11}$ consists of a part that depends linearly on time and a part that is independent of time and depends on the initial conditions of the trajectory. This informs us that the latter term is a phase. I think the fact that the last term in eqn (4.26) is a phase is clearer if the right-hand side is rewritten:

$$\frac{\left((gv_x)^2 + (hv_y)^2\right)t + \left(g^2 v_x x_0 + h^2 v_y y_0\right)}{\left((gv_x)^2 + (hv_y)^2\right)^{1/2}} = \frac{(gv_x)^2\left(t + \frac{x_0}{v_x}\right) + (hv_y)^2\left(t + \frac{y_0}{v_y}\right)}{\left((gv_x)^2 + (hv_y)^2\right)^{1/2}}. \tag{4.27}$$

Despite the algebraic complexity of the expressions for $(H_e')_{12}$ and $(H_e')_{11}$, it is comforting to know from eqn (4.15) that the eigenvalues can be expressed compactly.

6. General Expression

To obtain the general expression for the nonadiabatic transition probability, we will assess further the respective contributions of the two terms on the right-hand side of eqn (4.26). Our suspicion is that the term proportional to t enjoys a privileged status relative to the term to its right, as we do not anticipate that the phase will be important here. The reason can be traced back to a physically motivated assumption introduced in the 1932 paper by Zener, namely, $E_{12} = \alpha t$, where $E_{12} = E_1 - E_2$ is the energy difference between the diabats and α is a constant. The importance of diabats had been recognized at the time, but they had not yet been introduced formally. Zener referred to linear combinations of adiabatic wavefunctions. He assigned a time independent parameter to the coupling matrix element and a linear time variation to the energy difference E_{12}.

Meaningful comparison to the model presented here must use matrix elements that follow from the elimination of time behavior from the coupling matrix elements, as indicated in eqn (4.17'). The expression for $(H_e')_{11}$ given by eqn (4.26) and the fact that $(H_e')_{22} = -(H_e')_{11}$ (trace invariance) yield the following expression for the energy difference E_{12} on the trajectory

$$E_{12} = 2\left((gv_x)^2 + (hv_y)^2\right)^{1/2} t + 2\frac{g^2 v_x x_0 + h^2 v_y y_0}{\left((gv_x)^2 + (hv_y)^2\right)^{1/2}}. \tag{4.28}$$

This identifies α as the coefficient of t in the equation introduced by Zener, $E_{12} = \alpha t$. Again, the other term is a phase [see eqn (4.27)]. It appears in a phase factor $e^{i\mu}$ (where μ is a constant) that multiplies B_f. Time permitting this will be discussed later. It is not important here. The important point is that this α can be used in eqn (4.6), which was derived earlier and is reproduced below, and all that follows from it.

$$\ddot{B} + i\alpha t\dot{B} + |H_{12}|^2 B = \ddot{B} + iv|F_{12}|t\dot{B} + |H_{12}|^2 B = 0 \tag{4.6}$$

We now go straight to the answer via the substitutions described above. This yields

$$P(\varphi_2 \to \varphi_2) = P(\psi_2 \to \psi_1) = |B_f|^2 = \exp\left(-\frac{2\pi |H_{12}|^2}{\hbar\alpha}\right), \tag{4.29}$$

where:

$$|H_{12}|^2 = A_{so}{}^2 + \frac{(gh)^2\left(v_x y_0 - v_y x_0\right)^2}{\left(gv_x\right)^2 + \left(hv_y\right)^2}, \tag{4.30}$$

and

$$\alpha = 2\left((gv_x)^2 + (hv_y)^2\right)^{1/2} = v|F_{12}|. \tag{4.31}$$

Equations (4.29) – (4.31) apply to a given trajectory. It is necessary to average over an ensemble of trajectories appropriate to the system under consideration. If v_x and v_y are constant throughout a trajectory, then H_{12} and α are both constant, and evaluation of eqn (4.29) is easy. One weights the incident trajectories and sums their weighted probabilities. Now for a couple of examples.

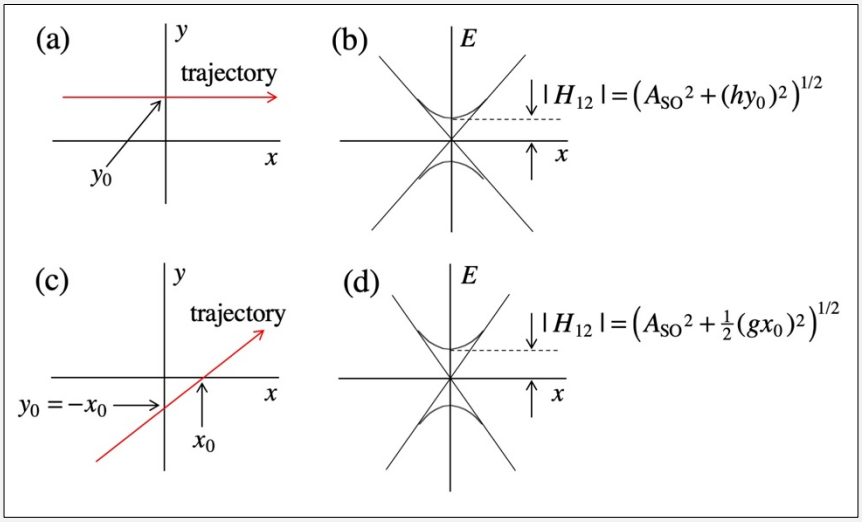


Figure 6. (a) A trajectory runs parallel to the x-axis at $y = y_0$. (b) Adiabats are separated by $2|H_{12}| = 2[A_{SO}^2 + (hy_0)^2]^{1/2}$ at $x = 0$ for the trajectory in (a). (c) The trajectory has nonzero components v_x and v_y, and it misses the origin. (d) The shapes are also hyperbolae for (c) and curves like it ($v_x \neq 0$, $v_y \neq 0$, missing the origin). When projecting onto the x-axis, the hyperbolae appear to rise more steeply than if they were plotted vs. the distance along the trajectory. To simplify matters, the conditions $|x_0| = |y_0|$ and $h = g$ have been used.

Figure 6(a) shows a straight-line trajectory in which motion is parallel to the x-axis at $y = y_0$. The origin is missed, so the $\pm|A_{so}|$ extrema of the hyperbolae are not accessed. From eqn (4.15) for the energies E_1 and E_2 of the upper and lower adiabats for the case of symmetric cones (no tilt), we see that the energy of the upper adiabat as a function of x is $E_1 = [A_{so}^2 + (gx)^2 + (hy_0)^2]^{1/2}$ [Fig. 6(b)]. The minimum value of E_1 is $[A_{so}^2 + (hy_0)^2]^{1/2}$ at $x = 0$, and the transition probability is

$$P = \exp\left(-\frac{2\pi\left(A_{so}^2 + (hy_0)^2\right)}{2\hbar v g}\right) \tag{4.32}$$

where $v_x = v$ has been used because $v_y = 0$. This expression submits to the geometric interpretation provided by Figs. 6(a) and 6(b). The diabats indicated by the straight lines in Fig. 6(b) make the situation analogous to the 1D case. The inclusion of spin-orbit interaction

has eliminated the intersection of the adiabats, and the second degree of freedom that is manifest here as hy_0 discriminates further against intersection.

In Figs. 6(c) and 6(d), x_0 and y_0 are each nonzero, and the trajectory follows a straight line. Imagine a hyperbola and a trajectory that does not pass through the origin. The shapes will be like the one shown in 6(b) except for two small things: (1) If projected onto the x or y axis, the $E(x)$ or $E(y)$ curves will appear to rise more steeply than along the direction of motion. The reason is that the cut through the hyperboloid is projected onto the x-axis. (2) The minimum will be offset from the origin because the cross sectional cut misses the origin. These features are seen in eqn (4.15): $E_{1(2)} = \pm[A_{so}{}^2 + (gx)^2 + (hy)^2]^{1/2}$. For the case shown in (c), $|g| = |h|$ and $y = x - x_0$.

Following minor algebra this results in

$$E_{1(2)} = \pm\left(A_{so}{}^2 + \tfrac{1}{2}(gx_0)^2 + 2g^2(x - \tfrac{1}{2}x_0)^2\right)^{1/2}. \tag{4.33}$$

At $x = \frac{1}{2}x_0$, the splitting between the adiabats is $2[A_{so}{}^2 + \frac{1}{2}(gx_0)^2]^{1/2}$. From here, it is not difficult to write the expression for the general case, *i.e.*, $|g| \neq |h|$, and $y = f(x)$:

$$E_{1(2)} = \pm\left(A_{so}{}^2 + \left(gx\right)^2 + \left(hf(x)\right)^2\right)^{1/2}. \tag{4.34}$$

This general elliptical paraboloid can be made to appear even simpler (circular paraboloid) by scaling (Chapter 3). Regardless, it is easily implemented.

The above exercise suggests that a swarm of classical trajectories can be used as a crude model of a quantum mechanical wave packet incident on a region of conical intersection. This presupposes that a reasonable incident wave packet can be obtained. This could be challenging for a polyatomic molecule that commences motion on, say, an upper adiabat and propagates in the high dimensional configuration space of the nuclear degrees of freedom before reaching the intersection region. The funneling engendered by gradients acting in the conical intersection region can channel flux toward the intersection. However, if the system spends too much time (say ~ 1 ps) roaming about outside the intersection region, it might enter the regime of chaotic dynamics, which would render the packet a mess.

Passing through an extremum

Referring to eqn (4.30), an interesting case is $v_x y_0 = v_y x_0$, in which case the hyperbola extrema $|H_{12}| = |A_{SO}|$ in Fig. 6 are accessed. They cannot be accessed exactly, but trajectories can come close enough to justify this approximation. Equations (4.25) and (4.26) then become

$$H_{12} = iA_{so} \tag{4.35}$$

$$H_{11} = \left((gv_x)^2 + (hv_y)^2\right)^{1/2}\left(t - x_0 / v_x\right). \tag{4.36}$$

The new representation is nearly adiabatic, i.e., except for the iA_{so} term. These forms enable eqn (4.11) to be used to obtain the nonadiabatic transition probability:

$$P(\psi_2 \to \psi_1) = \exp\left(-\frac{2\pi A_{so}{}^2}{2\left((gv_x)^2 + (hv_y)^2\right)^{1/2}}\right). \tag{4.37}$$

Non-Adiabatic Crossing of Energy Levels.

By Clarence Zener, National Research Fellow of U.S.A.

(Communicated by R. H. Fowler, F.R.S.—Received July 19, 1932.)

1. *Introduction.*

The crossing of energy levels has been a matter of considerable discussion.* The essential features may be illustrated in the crossing of a polar and homopolar state of a molecule.

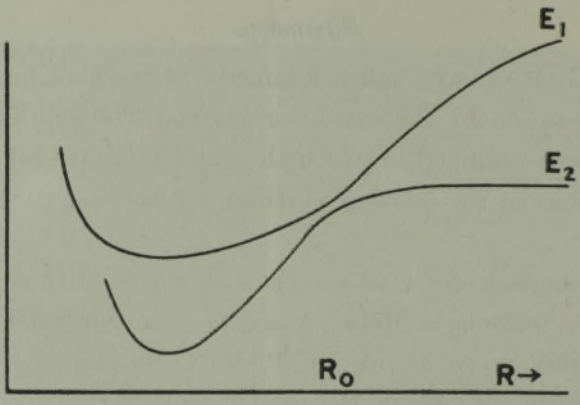


Fig. 1.—Crossing of polar and homopolar states.

Let $\psi_1(x/R)$, $\psi_2(x/R)$ be two electronic eigenfunctions of a molecule with stationary nuclei. Let these eigenfunctions have the property that for $R \gg R_0$, ψ_1 has polar characteristics, ψ_2 homopolar; while at $R \ll R_0$, ψ_2 has polar characteristics, ψ_1 homopolar. In the region $R = R_0$ these two eigenfunctions may be said to exchange their characteristics.

The adiabatic theorem tells us that if the molecule is initially in state ψ_2, and R changes infinitely slowly from $R \gg R_0$ to $R \ll R_0$, then the molecule will remain in state ψ_2. However, if R changes with a finite velocity, the final state $\psi(x/R)$ will be a linear combination

$$\psi(x/R) = A_1(R)\,\psi_1(x/R) + A_2(R)\,\psi_2(x/R). \qquad (1)$$

Neumann and Wigner (*loc. cit.*) have found the conditions for which

$$A_1 \sim 0, \qquad |A_2| \sim 1$$

and

$$|A_1| \sim 1, \qquad A_2 \sim 0,$$

* Hund, 'Z. Physik,' vol. 40, p. 742 (1927); Neumann and Wigner, 'Phys. Z.,' vol. 30, p. 467 (1929); Kemble and Zener, 'Phys. Rev.,' vol. 33, p. 536 (1929).

respectively, without however obtaining the explicit dependence of the A's upon the parameters of the system.

In order that the problem of obtaining this explicit dependence may be reduced to a precise soluble mathematical problem, it is desirable to specify the conditions of the transition as simply as possible, at the same time retaining the essential features.

Let ϕ_1, ϕ_2 be such linear combinations of ψ_1, ψ_2, that for all values of R, ϕ_1 has the characteristics which ψ_1 has at $R \gg R_0$, while ϕ_2 has the characteristics which ψ_2 has at $R \gg R_0$. In our molecular example, ϕ_1 will be a pure polar state, ϕ_2 a pure homopolar state for all internuclear distances. While ϕ_1, ϕ_2 can be made orthogonal, they will not satisfy the wave equation for fixed nuclei, rather

$$\left.\begin{aligned} H\phi_1 &= \varepsilon_1 \phi_1 + \varepsilon_{12} \phi_2 \\ H\phi_2 &= \varepsilon_{12} \phi_1 + \varepsilon_2 \phi_2 \end{aligned}\right\}. \tag{2}$$

The simplifications which will be made in order to obtain the explicit functions A_1, A_2, are the following :—

(*a*) $\varepsilon_{12}(R_0) \ll$ the relative kinetic energy of the two systems. Under this condition the motion of the centres of gravity of the two atoms, or in general of the two systems, may be treated as external parameters. That is, the variable R becomes a known function of time.

(*b*) The transition region is so small that in it we may regard $\varepsilon_1 - \varepsilon_2$ as a linear function of time, and $\varepsilon_{12}(R)$, $\phi_1(x/R)$, $\phi_2(x/R)$ as independent of time. This condition is satisfied provided $\varepsilon_{12}(R_0)$ is sufficiently small. Since only the characteristics in the transition region are of importance, this condition enables us to replace the physical problem by an ideal problem in which

$$\left.\begin{aligned} \frac{2\pi}{h}(\varepsilon_1 - \varepsilon_2) &= \alpha t \\ \dot{\varepsilon}_{12} = \dot{\phi}_1 &= \dot{\phi}_2 = 0 \end{aligned}\right\} \tag{3}$$

for all time.

If the relative velocity of the atoms is constant, assumption (*b*) leads to the relationship shown in fig. 2 between $\varepsilon_1(R)$, $\varepsilon_2(R)$ and the eigenwerte of ψ_1, ψ_2, namely $E_1(R)$, $E_2(R)$.

$E_1(R)$, $E_2(R)$ are hyperbolæ having $\varepsilon_1(R)$, $\varepsilon_2(R)$ as asymptotes. The closest distance between E_1 and E_2, *i.e.*, $E_1(R_0) - E_2(R_0)$, is given by $2\varepsilon_{12}(R_0)$.

2. *Analysis.*

In the analysis it has been found more convenient to use the linear combinations ϕ_1, ϕ_2 of the exact adiabatic solutions ψ_1, ψ_2 rather than these

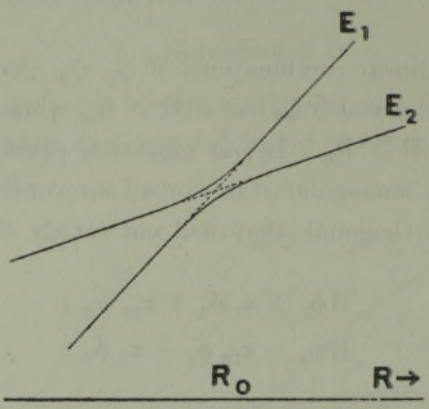


FIG. 2.—Crossing of energy levels in idealised problem. Full lines are adiabatic eigenwerte.

solutions themselves. Further, it has been found advantageous to start from the wave equation in the form

$$\left(\mathrm{H} - \frac{h}{2\pi i}\frac{\delta}{\delta t}\right)\left\{\mathrm{C}_1(t)\, e^{\frac{2\pi i}{h}\int \epsilon_1\, dt}\,\phi_1(x) + \mathrm{C}_2(t)\, e^{\frac{2\pi i}{h}\int \epsilon_2\, dt}\,\phi_2(x)\right\} = 0.$$

The relations (2) reduce this wave equation to two simultaneous first order differential equations in the C's.

$$\left.\begin{aligned} \frac{h}{2\pi i}\frac{\delta \mathrm{C}_1}{\delta t} &= \varepsilon_{12}\, e^{-\frac{2\pi i}{h}\int (\epsilon_1 - \epsilon_2)\, dt}\,\mathrm{C}_2. \\ \frac{h}{2\pi i}\frac{\delta \mathrm{C}_2}{\delta t} &= \varepsilon_{12}\, e^{\frac{2\pi i}{h}\int (\epsilon_1 - \epsilon_2)\, dt}\,\mathrm{C}_1. \end{aligned}\right\}. \qquad (4)$$

The boundary conditions under which these equations are to be solved must correspond to our knowledge that initially the system is in state ψ_2 or ϕ_2, which are equivalent when $\mathrm{R} \gg \mathrm{R}_0$. These conditions are thus

$$\mathrm{C}_1(-\infty) = 0. \qquad (5\text{A})$$

$$|\mathrm{C}_2(-\infty)| = 1. \qquad (5\text{B})$$

If we call $|\mathrm{A}_1(\mathrm{R} \ll \mathrm{R}_0)|^2$ of (1) the probability P of a non-adiabatic transition, then

$$\mathrm{P} = |\mathrm{C}_2(\infty)|^2 = 1 - |\mathrm{C}_1(\infty)|^2.$$

We thus need know only the asymptotic values of the solutions of (4).

Elimination of C_2 from (4) leads to the single equation

$$\frac{d^2C_1}{dt^2} + \left\{\frac{2\pi i}{h}(\varepsilon_1 - \varepsilon_2) - \frac{\dot{\varepsilon}_{12}}{\varepsilon_{12}}\right\}\frac{dC_1}{dt} + \left(\frac{2\pi\varepsilon_{12}}{h}\right)^2 C_1 = 0. \qquad (6)$$

Substitution of the assumption (3), together with the definition

$$f = \frac{2\pi\varepsilon_{12}}{h}$$

and the substitution

$$C_1 = e^{-\frac{\pi i}{h}\int(\epsilon_1-\epsilon_2)\,dt}\,U_1$$

reduces (6) to the Weber* equation

$$\frac{d^2U_1}{dt^2} + \left(f^2 - \frac{i\alpha}{2} + \frac{\alpha^2}{4}t^2\right)U_1 = 0.$$

This is thrown into the standard form

$$\frac{d^2U_1}{dz^2} + (n + \tfrac{1}{2} - \tfrac{1}{4}z^2)\,U_1 = 0,$$

by the substitutions

$$z = \alpha^{\frac{1}{2}}\,e^{-i\pi/4}\,t$$

$$n = if^2/\alpha.$$

The Weber function $D_{-n-1}(iz)$ is a particular solution of this equation which vanishes for infinite z along the directions $\infty \exp(-\frac{3}{4}\pi i)$ and $\infty \exp(-\frac{1}{4}\pi i)$. Hence the solution

$$U_1(z) = A_\pm\,D_{-n-1}(\mp iz), \qquad \alpha \gtrless 0,$$

satisfies the first boundary condition (5A).

The constants $A_\pm$ are determined from the asymptotic values

$$D_{-n-1}(iR\,e^{-\frac{1}{2}\pi i}) \underset{\text{R}\to\infty}{=\!=} e^{\frac{\pi}{4}(n+1)i}\,e^{iR^2/4}\,R^{-n-1},$$

$$D_{-n-1}(iR\,e^{\frac{1}{2}\pi i}) \underset{\text{R}\to\infty}{=\!=} e^{-\frac{\pi}{4}(n+1)i}\,e^{-iR^2/4}\,R^{-n-1},$$

by means of the second boundary condition (5B). We find

$$|A_+| = |A_-| = \gamma^{\frac{1}{2}}\,e^{-\pi\gamma/4},$$

where

$$\gamma = f^2/|\alpha|.$$

* Those properties of this equation, and of its solutions, which are used in this analysis are fully discussed in Whitaker and Watson's "Modern Analysis," pp. 347–349, 4th ed.

Summarising,

$$e^{i\frac{\pi a t}{h}} \mathop{\mathrm{L}}_{t\to\infty} \mathrm{C}_1(t) = \mathop{\mathrm{L}}_{z\to\infty \exp(-i\frac{1}{2}\pi)} \mathrm{U}_1(z) = \begin{cases} \gamma^{\frac{1}{2}} e^{-\pi\gamma/4} \mathop{\mathrm{L}}_{\mathrm{R}\to\infty} \mathrm{D}_{-n-1}(i\mathrm{R}e^{\frac{1}{2}\pi i}), & \alpha > 0. \\ \gamma^{\frac{1}{2}} e^{-\pi\gamma/4} \mathop{\mathrm{L}}_{\mathrm{R}\to\infty} \mathrm{D}_{-n-1}(i\mathrm{R}e^{\frac{1}{2}\pi i}), & \alpha < 0. \end{cases}$$

By use of the asymptotic values

$$\mathop{\mathrm{L}}_{\mathrm{R}\to\infty} \mathrm{D}_{-n-1}(i\mathrm{R}e^{\frac{1}{2}\pi i}) = e^{\frac{1}{2}\pi(n+1)i} e^{-i\mathrm{R}^2/4} \mathrm{R}^{-n-1} + \frac{\sqrt{2\pi}}{\Gamma(n+1)} e^{\frac{1}{2}\pi n i} e^{i\mathrm{R}^2/4} \mathrm{R}^n,$$

$$\mathop{\mathrm{L}}_{\mathrm{R}\to\infty} \mathrm{D}_{-n-1}(i\mathrm{R}e^{\frac{1}{2}\pi i}) = e^{-\frac{1}{2}\pi(n+1)i} e^{i\mathrm{R}^2/4} \mathrm{R}^{-n-1} + \frac{\sqrt{2\pi}}{\Gamma(n+1)} e^{\frac{1}{2}\pi n i} e^{-i\mathrm{R}^2/4} \mathrm{R}^n$$

we obtain

$$|\mathrm{C}_1(\infty)|^2 = \frac{2\pi\gamma e^{-\pi\gamma}}{\Gamma(i\gamma+1)\,\Gamma(-i\gamma+1)} = 2e^{-\pi\gamma}\sinh\pi\gamma$$

$$= 1 - e^{-2\pi\gamma}.$$

Therefore

$$\mathrm{P} = e^{-2\pi\gamma}, \qquad \gamma = \frac{2\pi}{h}\varepsilon_{12}^2 \Big/ \left|\frac{d}{dt}(\varepsilon_1 - \varepsilon_2)\right|.$$

Rosenkewitsch* states that Landau has obtained the formula

$$\mathrm{P} \sim e^{-\frac{\pi}{2hv}\frac{\Delta^2}{\mathrm{F}_1 - \mathrm{F}_2}}$$

where $\Delta = 2\varepsilon_{12}$, v is the relative velocity, and F_1, F_2 are the "forces" acting upon the two states. If the identification $\frac{d}{dt}(\varepsilon_1 - \varepsilon_2) = v(\mathrm{F}_1 - \mathrm{F}_2)$ can be made, the exponent of Landau's formula is too small by a factor of 2π.

3. *Discussion.*

Equation (6), with ε_1, ε_2, ε_{12}, as arbitrary functions of time, is the general equation for a transition probability between two electronic states, provided (*a*) all other states may be neglected; (*b*) the motion of the atoms may be taken as external parameters; (*c*) changes in the "unperturbed" wave functions ϕ_1, ϕ_2 may be neglected. Two cases are of particular interest. In one $\varepsilon_1 - \varepsilon_2 = \Delta\mathrm{E}$, a constant, and ε_{12} is a function having the general form of curve *a*, fig. 3. In the other $\varepsilon_1 - \varepsilon_2$ is a linear function, and ε_{12} is a constant.

* 'Phys. Z. U.S.S.R.,' vol. 1, p. 426 (1932).

An investigation* of the first case has revealed that the transition probability P satisfies the inequality

$$P \leqslant \left| \frac{\int_{-\infty}^{\infty} \varepsilon_{12}(t)\, e^{\frac{2\pi i}{h}\Delta E t}\, dt}{\int_{-\infty}^{\infty} \varepsilon_{12}(t)\, dt} \right|^2.$$

A more instructive form is obtained by introducing the variable $\xi = t/\tau$, where τ is the time of collision defined by

$$\tau \varepsilon_{12}(0) = \int_{-\infty}^{\infty} \varepsilon_{12}(t)\, dt.$$

Then

$$P \leqslant \left| \frac{\int_{-\infty}^{\infty} \varepsilon_{12}(\xi)\, e^{2\pi i \frac{\tau \Delta E}{h} \xi}\, d\xi}{\int_{-\infty}^{\infty} \varepsilon_{12}(\xi)\, d\xi} \right|^2. \tag{7}$$

When $\tau \Delta E/h > 1$, P is much smaller when ε_{12} is an analytic function than of the type of curve *b*, fig. 2. The question arises, would this difference in the two P's be eliminated merely by rounding off the corners of curve *b*, or must all

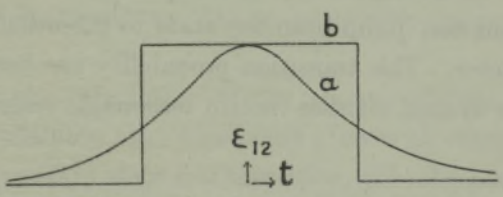


FIG. 3.—ε_{12} when $\varepsilon_1 - \varepsilon_2$ = a constant.

derivatives of ε_{12} be continuous ? We find the answer when we integrate the numerator of (7) by parts. Since ε_{12} vanishes at $\xi = \pm \infty$, an expansion of P in inverse powers of $(2\pi\tau\Delta E/h)$ is seen to start with the $-2n'$th power, where n is the order of the first discontinuous derivative of ε_{12}.†

The second case has been solved in the preceding section. The problem is illustrated in fig. 2.

It was found that the transition probability P was

$$P = e^{-\frac{\pi^2}{h}\Delta^2 \Big/ \left|\frac{d}{dt}(\varepsilon_1 - \varepsilon_2)\right|}$$

* N. Rosen and C. Zener, ' Phys. Rev.,' vol. 40, p. 502 (1932).

† The author is indebted to Professor Norbert Wiener for pointing out this relation.

where $\Delta = 2\varepsilon_{12}(0) =$ closest distance between the adiabatic eigenwerte E_1, E_2 of the system.

In both cases P depends upon the relative velocity v in nearly the same manner, namely

$$P \sim e^{-v_0/v}.$$

In collisions one measures an effective cross section Q. Let the transitional region occur about the interatomic distance R_0, then since v refers to the component of the relative velocity along the internuclear line, Q will be given by approximately

$$Q = \pi R_0^2 \int_0^{\pi/2} e^{-v_0/v \cos\theta} \sin\theta \, d\theta$$

$$= \pi R_0^2 \left\{ e^{-v_0/v} + \frac{v_0}{v} Ei(-v_0/v) \right\}.$$

Summary.

When a single parameter is varied adiabatically, two eigenwerte of a system may approach each other, and then recede, the corresponding eigenfunctions having exchanged their characters. If the parameter is varied with a finite velocity, the system may jump from one state to the other, thus not suffering a change of character. This transition probability has been rigorously calculated provided the system satisfies certain reasonable restrictions.